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PATENT SPECIFICATION

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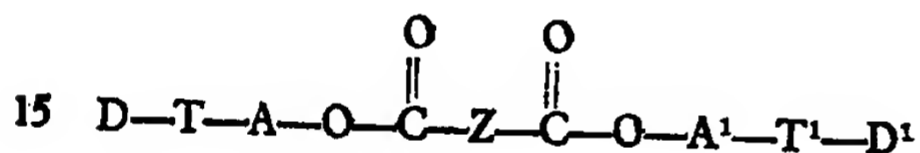
COMPLETE SPECIFICATION

New Polyazo Dyestuffs

5 We, IMPERIAL CHEMICAL INDUSTRIES LIMITED of Imperial Chemical House, Millbank, London, S.W.1, a British Company, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

10 This invention relates to new dyestuffs and more particularly it relates to new azo dyestuffs which are valuable for colouring textile materials.

According to the invention there are provided the new azo dyestuffs of the formula:



20 wherein A and A¹ each represent substituted or unsubstituted alkylene radicals containing from 2 to 6 carbon atoms and may be the same or different; D and D¹ each represent the residue of an azo dyestuff molecule and may be the same or different; T and T¹, which are directly attached to carbon atoms present in D and D¹, each represent a —SO₂—

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$$\begin{array}{c} R \\ | \\ -SO_2N- \end{array}$$
 or —SO₂N— group and may be the same or different; R represents a hydrogen atom or a substituted or unsubstituted hydrocarbon radical; and Z represents a direct link or a 30 divalent hydrocarbon radical which may contain substituents.

35 As examples of the substituted or unsubstituted alkylene radicals represented by A and A¹ there may be mentioned trimethylene, tetramethylene, propylene, β-hydroxytrimethylene and β:γ-butylenes radicals, but the preferred alkylene radical is the ethylene radical.

As examples of the substituted or unsubstituted hydrocarbon radicals represented by R [Price 4s. 6d.]

there may be mentioned alkyl radicals which 40 are preferably lower alkyl radicals such as methyl, ethyl, propyl and butyl radicals which may contain substituents such as methoxy and ethoxy groups, cycloalkyl radicals such as the cyclohexyl radical, and aryl radicals 45 for example monocyclic aryl radicals such as phenyl and tolyl radicals which may contain substituents such as chlorine atoms or methoxy groups.

50 As examples of the divalent hydrocarbon radicals represented by Z there may be mentioned divalent unsaturated aliphatic radicals for example divalent unsaturated lower aliphatic radicals such as the vinylene radical, 55 divalent aliphatic radicals for example divalent lower aliphatic radicals such as ethylene, trimethylene, tetramethylene, pentamethylene and hexamethylene radicals, divalent aryl radicals for example divalent monocyclic aryl radicals such as phenylene and tolylene radicals, and 60 divalent bicyclic aromatic radicals such as the diphenylene and naphthylene radicals, and divalent aromatic radicals of the formula:



wherein Q represents a bridging group such as 65 —CO—, —CH=CH— and —CH₂—, and the benzene rings may contain substituents such as chlorine atoms or methyl, methoxy, sulphonic acid, nitro and acetylamino groups.

70 Each of the groups represented by T and T¹ is directly attached to a carbon atom present in the residue of the azo dyestuff molecules represented by D and D¹. The said carbon atom may form part of an aryl radical present in the dyestuff molecule or may form 75 part of an alkyl chain which is directly attached to an aryl radical present in the dyestuff

molecule or may be attached to an aryl radical through a bridging atom or group. As examples of such bridging atoms or groups there may be mentioned —O—, —S—,

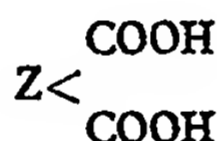
5 —NH—, —N-alkyl, —CO— and —COHN—.

The residues of the azo dyestuff molecules represented by D and D¹ may be the residues of monoazo or polyazo dyestuffs which preferably contain a water-solubilising group or groups such as a carboxylic acid, alkylsulphone or sulphonyl group and, above all, a sulphonic acid group. If desired the azo dyestuff molecules may also contain coordinately bound metal such as coordinately bound copper, chromium or cobalt.

According to a further feature of the invention there is provided a process for the manufacture of the new azo dyestuffs, as hereinbefore defined, which comprises treating 2 molecular proportions of a dyestuff compound of the formula:



or one molecular proportion of a dyestuff compound of the formula: D—T—A—OH and one molecular proportion of a different dyestuff compound of the formula D¹—T¹—A¹—OH, wherein A, A¹, D, D¹, T, and T¹ have the meaning stated above, with one molecular proportion of a halide of an acid of the formula:



wherein Z has the meaning stated above.

This process of the invention may be conveniently brought about by reacting the dyestuff compound or compounds with the halide of the said acid in a basic organic liquid such as pyridine, or in an organic liquid such as dimethylformamide or nitrobenzene in the presence of an acid-binding agent such as sodium carbonate or a basic organic liquid such as pyridine, preferably at a temperature between 20°C. and the boiling point of the organic liquid, and filtering off the precipitated dyestuff. If desired a liquid such as water or ether which is miscible with the organic liquid but which is not a solvent for the dyestuff, can be added before isolating the dyestuff.

As examples of halides of acids of the above formula which may be used in this process of the invention there may be mentioned fumaroyl chloride, succinyl chloride, adipoyl chloride, terephthaloyl chloride, isophthaloyl chloride, oxalyl chloride, cyclohexane-1:3-dicarboxylic acid chloride, 2:5-dichloroterephthaloyl chloride and 5-nitroisophthaloyl chloride.

The dyestuff compounds of the formula D—T—A—OH or D¹—T¹—A¹—OH where-

in T and T¹ each represent an —SO₂N— group, may be obtained by reacting the corresponding dyestuff compound containing an —SO₂Cl— group with an amine of the formula:

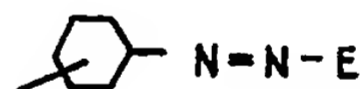


wherein A, A¹ and R have the meanings stated above. As examples of such amines there may be mentioned N-β-hydroxyethylamine, N-methyl-N-β-hydroxyethylamine, N-ethyl-N-β-hydroxyethylamine, N-phenyl-N-β-hydroxyethylamine and N-γ-hydroxy-n-propylamine.

The dyestuff compounds of the formula: D—T—A—OH or D¹—T¹—A¹—OH wherein T and T¹ each represent a —SO₂— group may be obtained by reacting the corresponding dyestuff compound or dyestuff intermediate containing a —SO₂H— group with a chloro compound of the formula: Cl.A—OH or Cl.A¹—OH wherein A and A¹ have the meanings stated above, and subsequently converting the dyestuff intermediate to the required dyestuff compound. As examples of such chloro compounds there may be mentioned ethylene chlorhydrin and 1-chloro-propanol-3.

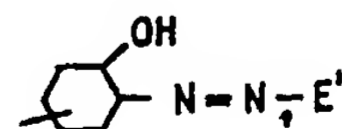
As specific examples of the residues of the azo dyestuff molecules represented by D and D¹ there may be mentioned the residues of dyestuffs of the following classes without however limiting the classes to those specifically described:

a) The dyestuffs of the formula:



wherein E represents the residue of a coupling component which is preferably a coupling component of the naphthol or 5-pyrazolone series which preferably contains a sulphonic acid group, and the benzene ring optionally contains further substituents.

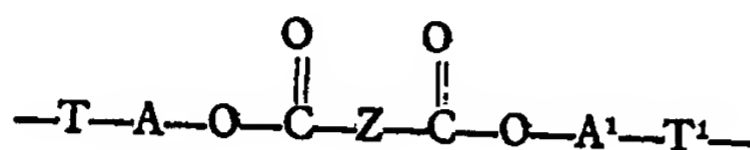
b) The copper complexes of the dyestuffs of the formula:



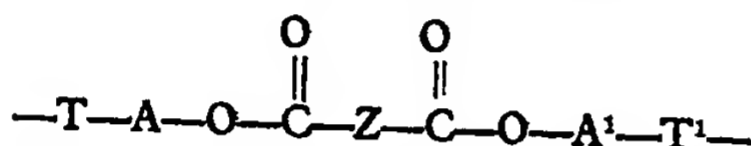
wherein E¹ represents the residue of a naphthol or 5-pyrazolone which is attached to the azo link in ortho or vicinal position to a hydroxy group and which preferably contains at least

one sulphonic acid group, and the benzene ring optionally contains further substituents.

According to a further feature of the invention there is provided a modified process for the manufacture of the new azo dyestuffs, as hereinbefore defined, which comprises tetrazotising an aromatic diamine which contains the group:



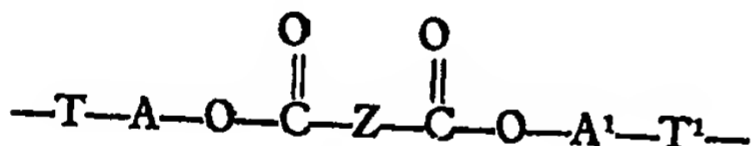
and coupling the tetrazo compound so obtained with 2 molecular proportions of a coupling component, or which comprises diazotising 2 molecular proportions of an aromatic amine and coupling the diazo compound so obtained with one molecular proportion of a coupling component which contains the group:



wherein A, A¹, T, T¹ and Z have the meanings stated above.

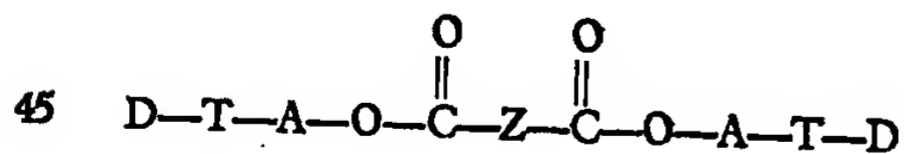
This modified process of the invention may be conveniently brought about by adding sodium nitrite to a solution or suspension of the aromatic diamine in a dilute aqueous solution of hydrochloric acid and adding the so-obtained aqueous solution or suspension of the diazo or tetrazo compound to an aqueous solution of the required coupling component and filtering off the azo dyestuff which is precipitated. If desired sodium chloride can be added to ensure complete precipitation of all the azo dyestuff.

The aromatic diamines or coupling components containing a



group may themselves be obtained by reacting the corresponding nitro compounds or coupling components respectively containing the groups —T—A—OH and —T¹—A¹—OH with a halide of an acid of the above formula and subsequently reducing the nitro groups to amino groups.

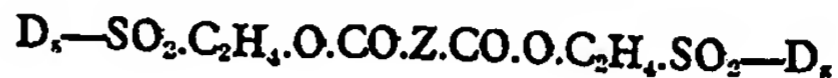
A preferred class of the new azo dyestuffs of the invention are the dyestuffs of the formula:



wherein A, D, T and Z have the meanings stated above.

As a specific example of a class of new azo dyestuffs of the invention which fall within

the preferred class there may be mentioned the azo dyestuffs of the formula:



wherein Z has the meaning stated above, each of the —SO₂— groups is attached directly to a carbon atom present in D₁, and D₁ represents the residue of an azo dyestuff molecule which contains at least one sulphonic acid group.

The new azo dyestuffs, as hereinbefore defined, are valuable for colouring natural and artificial textile materials for example textile materials comprising cotton, viscose rayon, regenerated cellulose, wool silk, cellulose acetate, polyamides, polyacrylonitrile, modified polyacrylonitrile and aromatic polyester fibres. For this purpose the azo dyestuffs can be applied to the textile materials by dyeing, padding or printing using printing pastes containing the conventional thickening agents or oil-in-water emulsions or water-in-oil emulsions, whereby the textile materials are coloured in bright shades possessing excellent fastness to wet treatments such as washing.

The new azo dyestuffs which contain water-solubilising groups, for example sulphonic acid and carboxylic acid groups, which render them soluble in water are particularly valuable for colouring cellulose textile materials. For this purpose the dyestuffs are preferably applied to the cellulose textile material in conjunction with a treatment with an acid-binding agent, for example sodium carbonate, sodium metasilicate, trisodium phosphate or sodium hydroxide, which may be applied to the cellulose textile material before, during or after the application of the dyestuff. Alternatively when the dyed textile material is to be subsequently heated or steamed a substance such as sodium bicarbonate or sodium trichloroacetate, which on heating or steaming liberates an acid-binding agent can be used.

For example the cellulose textile material can be coloured by treating the cellulose textile material with an aqueous solution or suspension of the acid-binding agent and then immersing the so-treated cellulose textile material in a dyebath comprising a solution of one or more of the new dyestuffs, as hereinbefore defined, at a temperature of between 0° and 100°C., removing the dyed cellulose textile material from the dyebath and if desired subjecting the dyed cellulose textile material to a treatment in a hot aqueous solution of soap.

If desired the cellulose textile material which has been treated with an aqueous solution or suspension of the acid-binding agent may be passed between rollers to remove excess aqueous solution or suspension of the acid-binding agent and/or dried before being treated with the aqueous solution of the said dyestuffs.

Alternatively the aqueous solution of the

dyestuff may be applied by padding to the cellulose textile material which has been treated with the acid-binding agent and the cellulose textile material then passed through rollers and subsequently subjected to the action of heat or steam. Alternatively the cellulose textile material can be padded with an aqueous solution of one or more of the new dyestuffs, as hereinbefore defined, which also contains an acid-binding agent, passing the so-treated cellulose textile material through rollers, then if desired drying the cellulose textile material at a suitable temperature, for example 70°C. and then subjecting the cellulose textile material to the action of heat or steam. Alternatively the cellulose textile material can be dyed by immersing it in a dyebath comprising an aqueous solution of one or more of the said dyestuffs which also contains an acid-binding agent, at a suitable temperature for example between 0° and 100°C. and thereafter removing the cellulose textile material from the dyebath, if desired subjecting it to a treatment in a hot aqueous solution of soap and finally drying the dyed cellulose textile material. Alternatively the aqueous solution of one or more of the said dyestuffs can be applied to the cellulose textile material by a dyeing or a padding method and the coloured cellulose textile material subsequently immersed in an aqueous solution or suspension of the acid-binding agent, preferably at a temperature between 50°C. and 100°C. or alternatively the coloured cellulose textile material may be padded with an aqueous solution or suspension of the acid-binding agent, the textile material dried and then subjected to the action of heat or steam. Alternatively the cellulose textile material can be dyed by immersing it in a dyebath comprising an aqueous solution of one or more of the said dyestuffs, preferably at a temperature between 20° and 100°C. and, after the textile material has absorbed some or all of the dyestuffs, adding an acid-binding agent and proceeding with the dyeing at the same or a different temperature.

The concentration of the acid-binding agent present in the aqueous solution or suspension or in the aqueous solution of the dyestuffs is not critical but it is preferred to use between 0.1% and 10% of the acid-binding agent based on the total weight of the aqueous solution or suspension. If desired the aqueous solution or suspension of the acid binding agent may also contain further substances, for example electrolytes such as sodium chloride and sodium sulphate.

The aqueous solution of the one or more of the said dyestuffs may also contain substances which are known to assist the application of dyestuffs to textile materials, for example sodium chloride, sodium sulphate, urea, dispersing agents, surface active agents, sodium alginate or an emulsion of an organic liquid,

for example trichloroethylene in water.

Alternatively the cellulose textile materials can be printed with a printing paste containing one or more of the new dyestuffs of the invention.

This may be conveniently brought about by applying a printing paste containing one or more of the said dyestuffs, to a cellulose textile material which has been impregnated with an acid-binding agent and thereafter subjecting the printed cellulose textile material to the action of heat or steam. Alternatively a printing paste containing one or more of the said dyestuffs and containing an acid-binding agent can be applied to the cellulose textile material and the printed cellulose textile material subsequently subjected to the action of heat or steam. Alternatively a printing paste containing one or more of the said dyestuffs can be applied to the cellulose textile material which is subsequently immersed in a hot aqueous solution or suspension of the acid-binding agent or alternatively the printed textile material is impregnated with an aqueous solution or suspension of the acid-binding agent and subsequently subjected to the action of heat or steam.

After applying the printing paste to the cellulose textile material the printed textile material may, if desired, be dried, for example at a temperature between 20° and 100°C. before the printed textile material is subjected to the action of heat or steam.

The cellulose textile material may be printed with the printing paste by any of the commonly known methods of applying printing pastes to textile materials, for example by means of roller printing, screen printing, block printing, spray printing or stencil printing. The printing pastes may also contain the commonly used adjuvants, for example urea, thickening agents, for example methyl cellulose, starch, locust bean gum, sodium alginate, water-in-oil emulsions, oil-in-water emulsions, surface active agents, sodium *m*-nitrobenzene sulphonate, and organic liquids, for example, ethanol.

At the conclusion of the dyeing and/or printing processes it is preferred to subject the so-coloured cellulose textile materials to a 'soaping' treatment, which may be carried out by immersing the coloured cellulose textile materials for a short time, for example 15 minutes, in a hot aqueous solution of soap and/or detergent, and subsequently rinsing the coloured cellulose textile material in water before drying it.

Those new azo dyestuffs which do not contain water-solubilising groups for example sulphonic acid, carboxylic acid, sulphonamide and acylsulphonamide groups are, in general, applied to textile materials in the form of an aqueous dispersion which may be obtained by gravel milling the dyestuff with water in the presence of a dispersing agent, for example

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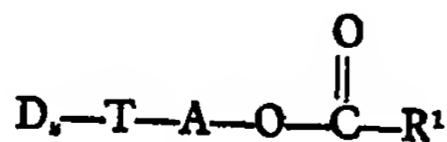
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the sodium salt of sulphonated naphthalene formaldehyde condensation products, sulpho-succinic acid esters, Turkey Red Oil, alkyl phenol/ethylene oxide condensation products, soap and similar surface active materials with or without protective colloids such as dextrin, British gum and water-soluble proteins. If desired the aqueous paste of the dyestuff so obtained may be dried to form a re-dispersible powder which may be converted to a non-dusting powder by any of the processes known for forming non-dusting powders.

The new azo dyestuffs, as hereinbefore defined, can be applied to nitrogen-containing textile materials such as wool and polyamide textile materials, from a mildly alkaline, neutral or acid dye bath. The dyeing process can be carried out at a constant or substantially constant pH, that is to say the pH of the dye bath remains constant or substantially constant during the dyeing process, or if desired the pH of the dye bath can be altered at any stage of the dyeing process by the addition of acids or acid salts or alkalis or alkaline salts. For example dyeing may be started at a dye bath pH of about 3.5 to 5.5 and raised during the dyeing process to about 6.5 to 7.5 or higher if desired. The dye bath may also contain substances which are commonly used in the dyeing of nitrogen-containing textile materials. As examples of such substances there may be mentioned ammonium acetate, sodium sulphate, ethyl tartrate, non-ionic dispersing agents such as condensates of ethylene oxide with amines, fatty alcohols or phenols, surface active cationic agents such as quaternary ammonium salts for example cetyl trimethylammonium bromide and cetyl pyridinium bromide and organic liquids such as *n*-butanol and benzyl alcohol.

When so applied to textile materials the new dyestuffs of the invention give colourations which have excellent fastness to wet treatments.

The new azo dyestuffs which contain water-solubilising groups are of particular importance for the colouration of cellulose textile materials as the said dyestuffs have excellent affinity for the cellulose textile materials and the resulting colourations have excellent fastness to wet treatments, such as washing, in that there is little or no staining of any white textile material which is present during the wet treatments. The azo dyestuffs of the invention have much higher affinity for cellulose textile materials than the corresponding known azo dyestuffs of the formula:



wherein A, D_x and T have the meanings stated above and R¹ represents an alkyl or aryl

radical which may contain a carboxylic or sulphonic acid group.

The invention is illustrated but not limited by the following Examples in which the parts and percentages are by weight:—

EXAMPLE 1

A solution of 0.7 part of sodium nitrite in 20 parts of water is added, during 15 minutes, to a stirred mixture of 3 parts of di-β-(3-amino - 4 - methoxyphenylsulphonylethyl)-terephthalate, 5 parts of a concentrated aqueous solution of hydrochloric acid, 25 parts of ice and 25 parts of water. The resulting mixture is stirred for 15 minutes at a temperature of 0°C. and 3 parts of sodium bicarbonate are then added. The mixture so obtained is then added, during 15 minutes, to a solution of 2.4 parts of 2-naphthol-6-sulphonic acid, 0.5 part of sodium hydroxide and 1.6 parts of sodium carbonate in 25 parts of water at a temperature of 5°C. The mixture is stirred for 2 hours at this temperature, 10 parts of sodium chloride are then added and the precipitated dyestuff is filtered off and dried.

When applied to cellulose textile materials in conjunction with a treatment with an acid-binding agent the dyestuff yields yellowish-red shades which have excellent fastness to wet treatments.

The di - β - (3 - amino - 4 - methoxyphenylsulphonylethyl)terephthalate used in the above Example may be obtained as follows:

A mixture of 6 parts of terephthaloyl chloride, 10 parts of pyridine, 16 parts of 2-nitroanisole-4-β-hydroxyethylsulphone and 300 parts of toluene is stirred at the boil under a reflux condenser for 24 hours. The mixture is then cooled to 20°C. and the precipitated di - β - (3 - nitro - 4 - methoxyphenylsulphonylethyl)terephthalate is filtered off, washed with water and dried. The product when crystallised from an aqueous solution of dimethylformamide melts at 210° to 211°C.

5 parts of Raney Nickel catalyst are added to a solution of 10 parts of di - β - (3 - nitro - 4 - methoxyphenylsulphonylethyl)terephthalate in 100 parts of dimethylformamide and the resulting mixture is stirred in an autoclave at a temperature of 25°C. and in the presence of hydrogen until reduction is complete. The mixture is then filtered and the filtrate so obtained is poured into 400 parts of water. The precipitated solid is then filtered off, washed with water and dried. After crystallisation from acetic acid the di-β(3-amino-4-methoxyphenylsulphonylethyl)terephthalate melts at 186° to 188°C. On analysis the product is found to contain 52.5% of carbon, 4.8% of hydrogen, 4.6% of nitrogen and 11.0% of sulphur. C₂₆H₂₈O₁₀N₂S₂ requires 52.7% of carbon, 4.7% of hydrogen, 4.7% of nitrogen and 10.8% of sulphur.

The following Table gives further Ex-

amples of new azo dyestuffs of the invention which are obtained when the 2.4 parts of 2-naphthol-6-sulphonic acid used in Example 1 are replaced by equivalent amounts of the coupling components listed in the second column of the Table. The third column of the Table indicates the shades obtained when the dyestuffs are applied to cellulose textile materials in conjunction with a treatment with an acid-binding agent. 10

Example	Coupling Component	Shade
2	2-naphthol-3:6-disulphonic acid	Red
3	1-(2'-chloro-4'-sulpho-6'-methyl-phenyl)-3-methyl-5-pyrazolone	Yellow
4	2-acetylamino-5-naphthol-7-sulphonic acid	Orange
5	1-naphthol-5-sulphonic acid	Red
6	1-amino-8-naphthol-3:6-disulphonic acid	Reddish-violet

EXAMPLE 7

A mixture of 9.2 parts of the azo compound which is obtained by coupling diazotised 3-amino-4-methoxyphenyl- β -hydroxyethylsulphone with 2-naphthol-6-sulphonic acid in alkaline medium, 2 parts of terephthaloyl chloride and 100 parts of pyridine is stirred at the boil under a reflux condenser for 22 hours. The mixture is then cooled to 20°C. 500 parts of diethylether are added and the precipitated dyestuff is filtered off, washed with diethylether and dried. The dyestuff so obtained is identical with the dyestuff of Example 1.

EXAMPLE 8

In place of the 2 parts of terephthaloyl chloride used in Example 7 there are used 2 parts of isophthaloyl chloride whereby a similar dyestuff is obtained.

EXAMPLE 9

A mixture of 10.6 parts of the copper complex of 2-(2'-hydroxy-5'- β -hydroxyethylsulphonylphenylazo)-1-naphthol-4-sulphonic acid, 2 parts of terephthaloyl chloride and 100 parts of pyridine is stirred for 22 hours at the boil under a reflux condenser. The mixture is then cooled to 20°C., 500 parts of diethylether are added, and the dyestuff which is precipitated is filtered off, washed with diethylether, and dried.

When applied to cellulose textile materials in conjunction with a treatment with an acid-binding agent the dyestuff yields red shades which possess very good fastness to washing and to light.

The copper complex used in the above Example may itself be obtained by coupling diazotised 2-aminophenol-4- β -hydroxyethylsulphone with 1-naphthol-4-sulphonic acid,

and subsequently heating with an aqueous solution of copper acetate.

EXAMPLE 10

In place of the 10.6 parts of the copper complex used in Example 9 there are used 10.3 parts of 1-[3'- β -hydroxyethylsulphonylphenyl]-3-methyl-4-(6'-sulphonaphth-2'-ylazo)-5-pyrazolone (which is obtained by coupling diazotised 2-naphthylamine-6-sulphonic acid with 1-[3'-(β -hydroxyethylsulphonylphenyl)-3-methyl-5-pyrazolone] whereby a dyestuff is obtained, which, when applied to cellulose textile materials in conjunction with a treatment with an acid-binding agent yields orange shades which are fast to wet treatments.

EXAMPLE 11

In place of the 10.6 parts of the copper complex used in Example 9 there are used 9.0 parts of 2-[4'-(N- β -hydroxyethylsulphamyl)phenylazo]-1-naphthol-4-sulphonic acid (which may be obtained by coupling diazotised aniline-4-sulphon-N-(β -hydroxyethyl)amide with 1-naphthol-4-sulphonic acid) whereby a dyestuff is obtained, which, when applied to cellulose textile materials in conjunction with a treatment with an acid-binding agent, yields reddish-orange shades which are fast to wet treatments.

The following Table gives further Examples of the new azo dyestuffs which are obtained when the 3 parts of di- β -(3-amino-4-methoxyphenylsulphonyl)terephthalate used in Example 1 are replaced by equivalent amounts of the diamines listed in the second column of the Table, and/or the 2.4 parts of 2-naphthol-6-sulphonic acid used in Example 1 are replaced by equivalent amounts of the

coupling components listed in the third column of the Table. The fourth column of the Table indicates the shades obtained when the dye-

stuffs are applied to cellulose textile materials in conjunction with a treatment with an acid-binding agent.

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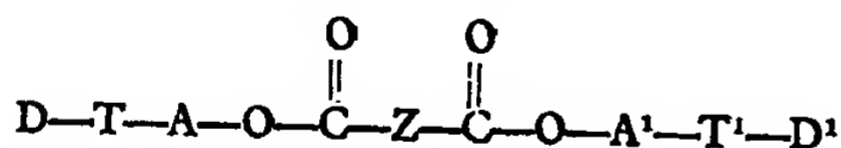
Example	Diamine	Coupling Component	Shade
12	di-β-(3-amino-4-methoxyphenylsulphonylethyl)oxalate	2-naphthol-3:6-disulphonic acid	Red
13	di-β-(3-amino-4-methoxyphenylsulphonylethyl)succinate	— do —	— do —
14	di-β-(3-amino-4-methoxyphenylsulphonylethyl)fumarate	— do —	— do —
15	di-β-(3-amino-4-chlorophenylsulphonylethyl)terephthalate	2-naphthol-6-sulphonic acid	Orange

The di-β-(3-amino-4-methoxyphenylsulphonylethyl)oxalate, di-β-(3-amino-4-methoxyphenylsulphonylethyl)fumarate and di-β-(3-amino-4-methoxyphenylsulphonylethyl)succinate used in the above Examples may be obtained by the method described in Example 1 for the preparation of di-β-(3-amino-4-methoxyphenylsulphonylethyl)terephthalate except that the terephthaloyl chloride is replaced by equivalent amounts of oxalyl chloride, fumaroyl chloride or succinyl chloride respectively.

The di-β-(3-amino-4-chlorophenylsulphonylethyl)terephthalate used in the above Examples may be obtained by the method described in Example 1 for the preparation of di-β-(3-amino-4-methoxyphenylsulphonylethyl)terephthalate except that the 2-nitroaniso-4-β-hydroxyethylsulphone is replaced by an equivalent amount of 2-nitrochlorobenzene-4-β-hydroxyethylsulphone.

WHAT WE CLAIM IS:—

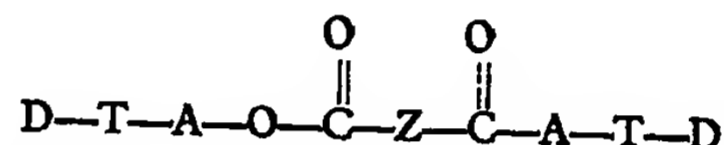
1. New azo dyestuffs of the formula:



wherein A and A¹ each represent substituted or unsubstituted alkylene radicals containing from 2 to 6 carbon atoms and may be the same or different; D and D¹ each represent the residue of an azo dyestuff molecule and may be the same or different; T and T¹, which are directly attached to carbon atoms present in D and D¹, each represent a

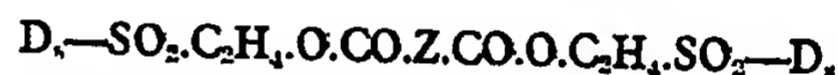
—SO₂— or —SO₂N— group and may be the same or different; R represents a hydrogen atom or a substituted or unsubstituted hydrocarbon radical; and Z represents a direct link or a divalent hydrocarbon radical which may contain substituents.

2. New azo dyestuffs of the formula:



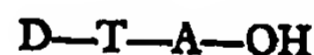
wherein A, D, T and Z have the meanings stated in Claim 1.

3. New azo dyestuffs of the formula:

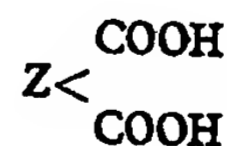


wherein Z has the meaning stated in Claim 1, each of the —SO₂— groups is directly attached to a carbon atom present in D₁, and D₂ represents the residue of an azo dyestuff molecule which contains at least one sulphonie acid group.

4. Process for the manufacture of the new azo dyestuffs, as claimed in Claim 1, which comprises treating two molecular proportions of a dyestuff compound of the formula:



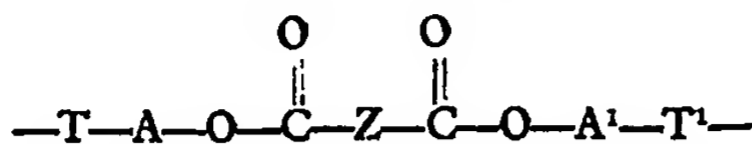
or one molecular proportion of a dyestuff compound of the formula: D-T-A-OH and one molecular proportion of a different dyestuff compound of the formula D¹-T¹-A¹-OH, wherein A, A¹, D, D¹, T, and T¹ have the meanings stated in Claim 1, with one molecular proportion of a halide of an acid of the formula:



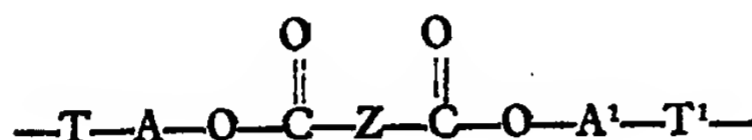
wherein Z has the meaning stated in Claim 1.

5. Process for the manufacture of the new azo dyestuffs as claimed in Claim 1, which comprises tetrazotising an aromatic diamine which contains the group:

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- 5 and coupling the tetrazo compound so obtained with 2 molecular proportions of a coupling component, or which comprises diazotising 2 molecular proportions of an aromatic amine and coupling the diazo compound so obtained with one molecular proportion of a coupling component which contains the group:



- 10 wherein A, A', T, T' and Z have the meanings stated in Claim 1.

6. Process for the manufacture of new azo

dyestuffs as hereinbefore particularly described especially with reference to any of the foregoing Examples.

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7. Process for colouring textile materials which comprises treating the textile material with a dyestuff as claimed in any of Claims 1 to 3.

8. Process as claimed in Claim 7 wherein the textile material is a cellulose textile material.

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9. Process as claimed in Claim 8 wherein the treatment of the cellulose textile material is carried out in conjunction with a treatment with an acid-binding agent, which may be applied to the cellulose textile material before, during or after the application of the dyestuff.

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